

Muddy waters: temporal variation in sediment discharging from a karst spring

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Abstract

Karst aquifers are capable of transporting and discharging large quantities of suspended sediment, which can have an important impact on water quality. Here we present the results of intensive monitoring of sediment discharging from a karst spring in response to two storm events, one following a wet season and the other following a dry season; we describe temporal changes in total suspended solids (TSS), mineralogy, and particle size distribution. Peak concentrations of suspended sediment coincided with changes in aqueous chemistry indicating arrival of surface water, suggesting that much of the discharging sediment had an allochthonous origin. Concentrations of suspended sediment peaked 14–16 h after rainfall, and the bulk of the sediment (approximately 1 metric ton in response to each storm) discharged within 24 h after rainfall. Filtered material included brightly colored fibers and organic matter. Suspended sediments consisted of dolomite, calcite, quartz, and clay. Proportions of each mineral constituent changed as the aquifer response to the storm progressed, indicating varying input from different sediment sources. The hydraulic response of the aquifer to precipitation was well described by changes in parameters obtained from the particle size distribution function, and corresponded to changes seen in TSS and mineralogy. Differences between storms in the quantity and mineralogy of sediment transported suggest that seasonal effects on surface sediment supply may be important. The quantity of sediment discharging and its potential to sorb and transport contaminants indicates that a mobile solid phase should be included in contaminant monitoring and contaminant transport models of karst. Temporal changes in sediment quantity and characteristics and differences between responses to the two storms, however, demonstrate that the process is not easily generalized. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Water quality is profoundly impacted by mobile particulates. Sediment itself is often considered a contaminant, and also can concentrate and transport other contaminants. In karst aquifers, flow through

conduits may be turbulent, enabling the rapid transport of sediment in a wide range of sizes. Sediment in karst is of concern: its deposition within the aquifer decreases aquifer permeability, fills in wells, and interferes with pump performance; it impairs the esthetic appearance of spring water and may destroy species habitat; and it can act as a vector for nutrient, contaminant, or bacterial transport.

The presence of mobile sediments in karst has been recognized for several decades (Bretz, 1942). White (1988) cites rapid facies changes in cave sediments as

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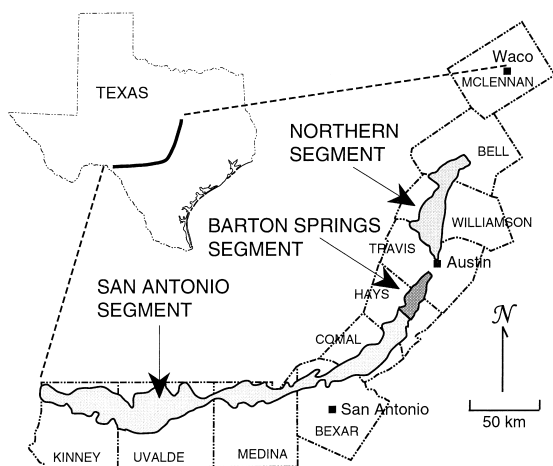


Fig. 1. The three segments of the Edwards (Balcones Fault Zone) aquifer.

evidence of stream flow “subject to large annual fluctuations” but adds that “little is known of the actual transport rates (of sediments) or how the loads are distributed among flood pulses of various magnitudes”. The limited number of investigations of sediment in karst systems have included dating of sediments using radionuclides (Murray et al., 1993),

calculation of hydraulic conditions in groundwater conduits based on sediment grain size (Gale, 1984), and determination of sediment source based on infrared spectroscopy (White, 1977). The importance of sediment in karst from an environmental standpoint is only beginning to be appreciated. Ryan and Meiman (1996) investigated temporal variations in nonpoint source pollutants in spring flow, but their description of mobile particulates was limited to determination of total suspended solids (TSS) concentrations. Atteia and Kozel (1997) describe differences in particle size distributions at two karst springs, identifying both colloidal and larger size particle populations, and discuss the potential importance of colloid-mediated contaminant transport in karst.

Here we focus on temporal changes in geochemical characteristics of particulates discharging from a major karst spring in response to precipitation, and relate them to sediment source and potential for contaminant transport. The karst aquifer investigated is the Barton Springs segment of the Edwards aquifer (referred to here as the Barton Springs aquifer) in central Texas (Fig. 1), one of the most rapidly urbanizing regions in the United States. Groundwater from the Barton Springs aquifer discharges from Barton Springs, the fourth largest spring in Texas (Brune,

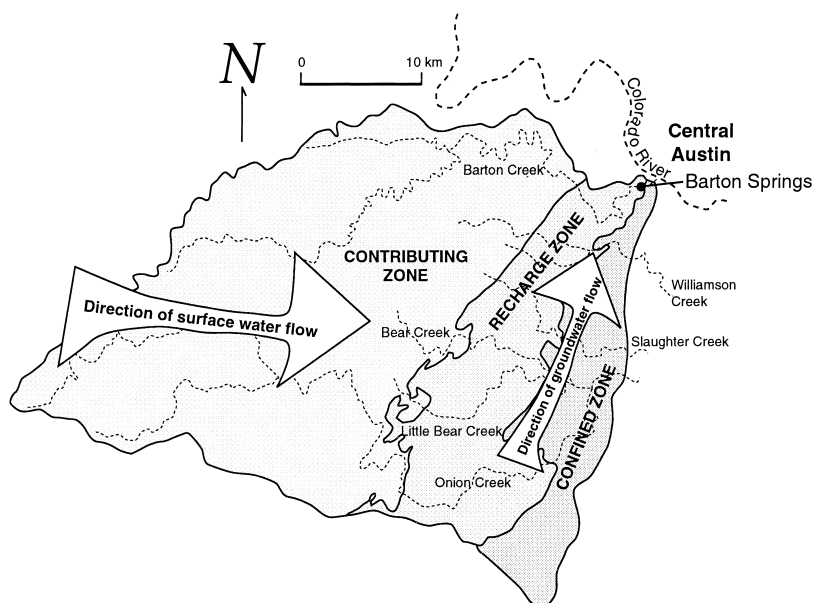


Fig. 2. The Barton Springs aquifer and contributing zone.

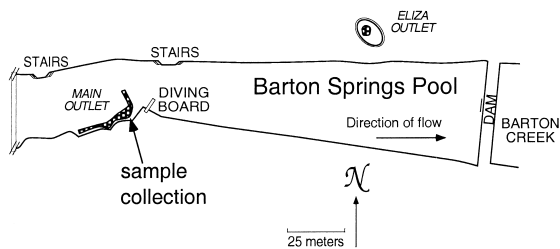


Fig. 3. Diagram of Barton Springs pool.

1981), located within sight of downtown Austin's highrises (Fig. 2). Increased amounts of sediment in wells and springs in the Barton Springs aquifer have been documented over the last decade, and elevated levels of arsenic, lead, and aluminum are associated with sediments in a number of well samples (Hauwert and Vickers, 1994). Barton Springs water quality is important for a number of reasons. First, the major set of spring orifices feeds a 225 m-long swimming pool enjoyed by over 340,000 people per year; Barton Springs Pool is a significant addition to Austin's quality of life and an important tourist attraction. Second, Barton Springs provides a part of Austin's municipal water supply: water from Barton Springs discharges into the Colorado River approximately 0.6 km upstream of one of Austin's three water supply plants, contributing at times more than 90% of flow in this section of the Colorado River (Slade et al., 1986). Third, the Barton Springs Salamander (*Eurycea sosorum*), listed as an endangered species by the US Fish and Wildlife Service, lives only in Barton Springs and is extremely vulnerable to changes in water quality (US Fish and Wildlife Service, 1997).

For this study, suspended sediment was collected at Barton Springs at hourly intervals following two rain events: one at the end of a period of normal rainfall, and one at the end of a six-month period of little rain. Temporal changes in the concentration, composition, and size distribution of the sediment in response to the storm pulse were investigated and related to sediment source, seasonal effects, and implications for contaminant transport.

2. Hydrogeologic setting

The unusual hydrogeologic regime of the Barton

Springs aquifer has been shaped by the depositional and structural history of the Central Texas area. The aquifer extends southwest of Austin, Texas across 391 km², and is bounded to the north by the Colorado River, to the east by a "bad water line" beyond which the water contains more than 1000 mg/l dissolved solids, to the south by a groundwater divide, and to the west by the fault-controlled interruption of the Edwards Limestone (Fig. 2). Although surface flow across the aquifer's watershed is generally from west to east, groundwater flows predominantly NNE, and approximately 90% discharges from Barton Springs.

The Barton Springs aquifer is composed of the Edwards and Georgetown Limestones. The Edwards Group conformably overlies the Glen Rose Limestone, and is unconformably overlain by the Georgetown Limestone, which is in turn overlain by the relatively impermeable Del Rio Clay. Karstification of Cretaceous lagoonal and rudist reef deposits during periods of subaerial exposure created lateral porosity along bedding planes (Rose, 1972; Maclay and Small, 1984). Later vertical displacement along NNE-trending high-angle normal faults allowed infiltration of meteoric water and creation of vertical porosity during the Oligocene–Miocene epochs (Slade, 1986). These NNE-trending faults comprise the Balcones Fault Zone and are responsible for the structurally controlled direction of subsurface flow.

The Barton Springs aquifer and its watershed are divided into three areas: the contributing zone, the recharge zone, and the artesian zone (Fig. 2). The contributing zone, which covers 684 km², is that portion of the watershed where the Glen Rose Limestone outcrops; surface flow from this area ultimately recharges the aquifer. The outcrop of the Edwards and Georgetown Limestones defines the 233 km² recharge zone. The artesian zone (or confined zone) is the eastern part of the aquifer, covering 158 km², where the Edwards and Georgetown Limestones are confined by the relatively impermeable Del Rio Clay. Seasonal fluctuations in the water table cause a narrow strip of this portion adjacent to the recharge zone to be under water table conditions at some times. Most surface water flows east across the contributing zone via one of six creeks (Barton, Williamson, Slaughter, Little Bear, Bear, and Onion). Once water in these creeks crosses onto the recharge zone, it infiltrates into the aquifer through sinkholes and fractures in

the creekbeds, providing an estimated 85% of total aquifer recharge (Slade et al., 1986).

Barton Springs actually consists of four major sets of hydrologically connected springs: Eliza Springs, Old Mill Springs, Upper Barton Springs, and Main Springs, the largest of the four. In 1910 a dam was built just downstream of Main Springs, creating Barton Springs Pool (Slade et al., 1986) (Fig. 3). Barton Creek, when flowing, is routed around the pool by a bypass structure. Only under extreme conditions does creekflow overwhelm the capacity of the bypass structure and flow into the pool; this did not occur during the period of this study.

Impoundment of spring flow by the pool dam places an artificial head above Main Springs. When the pool is full, the depth of water over the principal spring orifice is about 4.5 m; when the dam gates are removed (“drawdown”), water depth at the same point is about 3.2 m and spring discharge (Q) increases as a result of the sudden change in hydraulic gradient. The pool level is lowered by City of Austin (COA) staff at least weekly and after rainfall for pool cleaning. The USGS has developed two separate rating curves for Barton Springs: one for use when the pool is full and the other for use when the pool is drained. The rating curves were constructed by correlating spring Q with water level in a well located 61 m from Main Springs, and are discussed in detail by Senger (1983) and Slade et al., (1986). Based on the USGS rating curves, during low-flow conditions drawdown causes an increase in spring Q from less than 0.57 to 1.25 m³/s, and during average flow from 1.42 to 1.93 m³/s.

Barton Springs water has, overall, a calcium–magnesium bicarbonate chemistry (Senger, 1983; Slade et al., (1986)). When aquifer levels are low, concentrations of primarily sodium and chloride and to a lesser extent sulfate and magnesium increase, which Slade et al., (1986) attribute to encroachment of the bad water zone. COA data (unpublished) show an increase in specific conductance (SC) of spring water following pool drawdown ranging from 5% under high-flow conditions to 12% under low-flow conditions. The maximum increase occurs 12 h after the pool is drained; initial conditions are recovered 12–13 h after the gates are replaced and the pool has filled, which requires from one to several hours, depending on Q .

Although in general water quality at Barton Springs is considered good, there have been occurrences of contamination across the Barton Springs aquifer. Petroleum hydrocarbons, pesticides, arsenic, and lead have been detected in water samples from aquifer wells and small springs (Hauwert and Vickers, 1994); low levels of tetrachlorethylene have been detected in Barton Springs water (R.M. Slade, unpublished data); high levels of polycyclic aromatic hydrocarbons (PAHs) were found in sediments in Barton Creek and Barton Springs pool in the months following a major storm (City of Austin, unpublished data). Spills of hazardous materials in the aquifer region reported to the Texas Water Commission from 1986 to 1992 included gasoline and diesel fuels, pesticides, trichloroethane, and perchloroethene (US Fish and Wildlife, 1997). Many of the contaminants listed above sorb onto solid surfaces in concentrations orders of magnitude greater than that of their equilibrium concentration in the aqueous phase. The degree to which this occurs is a function of the individual contaminant and the organic carbon content, specific surface area, and mineralogy of the particulate. Both neutral and ionizable organic chemicals can partition into organic matter and adsorb to polar mineral surfaces (Schwarzenbach et al., 1993), while metallic ions are adsorbed into clay layers and onto oxide and carbonate surfaces by ion exchange (McCarthy and Zachara, 1989). Thus mobile particulates in the Barton Springs aquifer may be playing an important role in the concentration and transport of contaminants.

3. Methodology

3.1. Sample collection

Hourly samples for sediment and water analyses were collected from an orifice of Main Springs following two high-intensity storm events and one drawdown (nonstorm) event. The collection orifice, located to the south of and approximately 2 m higher than the principal orifice, is the sample site used by both the COA and the US Geological Survey for analyses of Barton Springs water (Fig. 3).

Spring discharge was calculated using the USGS rating curves. From July 1995 to March 1997 the

temporary addition of a mechanical stop in the monitoring well bore prevented monitoring of water level during drawdown (M. Dorsey, personal communication). For this study, therefore, discharge during pool drawdown was estimated based on drawdown discharge for pre-July 1995 periods of a similar aquifer level.

Samples for sediment and water chemistry analyses were collected in 20-l polyethylene containers (two per sample) by submerging the container in the springflow. For the storm events, aliquots for anion and cation analyses were removed after transport to the laboratory, and for the drawdown event were filtered onsite and stored on ice. All aliquots were filtered to 0.22 μm , and cation samples were acidified with concentrated nitric acid to pH 3; samples were kept refrigerated until analysis. One-liter samples were removed for measurement of TSS. The particulate fraction in the remaining sample (approximately 38.5 l) was concentrated by in-line centrifugation: sample was pumped at a steady rate of 120 ml/min through a Servall in-line system rotating at 6000 rpm; residence time was 3.3 min, corresponding to collection of the $> 0.3\text{-}\mu\text{m}$ fraction.

The first rain event ("Storm 1") occurred on 31 October–1 November 1995. On 31 October, 27.9 mm of rain fell between 4:00 and 6:00 p.m. At 5:30 p.m. water in the pool was still very clear, with good visibility to the bottom (about 4 m). The dam gates were lowered at 10 p.m. The following morning 57.1 mm of rain fell between 1:00 and 6:00 a.m., with most of it falling between 1:00 and 2:00 a.m. and between 5:00 and 6:00 a.m. At 8:00 a.m. water in the pool was noticeably turbid and the bottom was no longer visible. At 5:00 a.m. the dam gates were reinstalled and the pool level allowed to rise; the gates were again removed at 10:00 a.m. and not reinstalled until 5:30 a.m. on 2 November.

Storm 2, six months later, represents the first significant rainfall following Storm 1. On 30 May 1996, 44 mm of rain fell between 3:00 and 4:00 a.m., daylight savings time ("Storm 2"). Between Storms 1 and 2, the only precipitation greater than 10 mm occurred on 5 April when 24 mm of rain fell. The day before Storm 2 pool water was clear; by 7:00 a.m. on 30 May pool water had become cloudy. The pool was lowered at 9:15 a.m. on 30 May and allowed to fill again at 7:00 p.m. the same day.

A drawdown event was sampled 18–19 July 1996. Spring samples were collected hourly for 24 h beginning 15 min before drawdown at 8:00 p.m. There had been no rainfall the three weeks previous except for 1.0 mm of rain on 10 July. The dam gates were reinstalled at 5:00 a.m. on 19 July, then removed again at 10 p.m. the same day.

3.2. Analyses

Suspended sediment samples were analyzed for mineralogy and particle size distribution; water samples were analyzed for pH, SC, turbidity, TSS, and cation and anion concentrations. All analyses were performed at the University of Texas at Austin Department of Geological Sciences, with the exception of the particle size distribution analyses, which were performed by the Environmental and Water Resources Engineering area of the Department of Civil Engineering, University of Texas at Austin.

Mineralogy was analyzed by powder X-ray diffraction with a Siemens D-500 diffractometer, using a 0.02 2θ step and a 2-s time count. The data were interpreted as described in Lynch (1997).

Total suspended solids were determined by weight difference after vacuum filtration. One-liter samples were passed through 0.22- μm , 47-mm diameter filters (MSI MicronSep) and allowed to dry for 48 h. The filters were weighed before and after filtration. The average difference in weight of three filters through which distilled deionized water had been passed was subtracted from the computed sample weight. The filters were later examined under a binocular microscope for visual identification of particulates.

Particle size distributions were determined by the Coulter Counter system (Coulter Multizer, Coulter Electronics). The Coulter Counter measures the number and size of particles suspended in an electrolyte solution based on changes in resistance as the particles are pulled through a small aperture. Fifteen, 100, and 280 μm apertures with 4%, 2%, and 2% NaCl solutions, respectively, were used for Storm 1, and 30, 100, and 280 μm apertures with a 2% NaCl solution were used for Storm 2.

Turbidity, pH, and SC of spring water were measured in situ using a Horiba Model U-10. Concentrations of anions were determined by single-column ion chromatography (Waters Ion Chromatograph) by

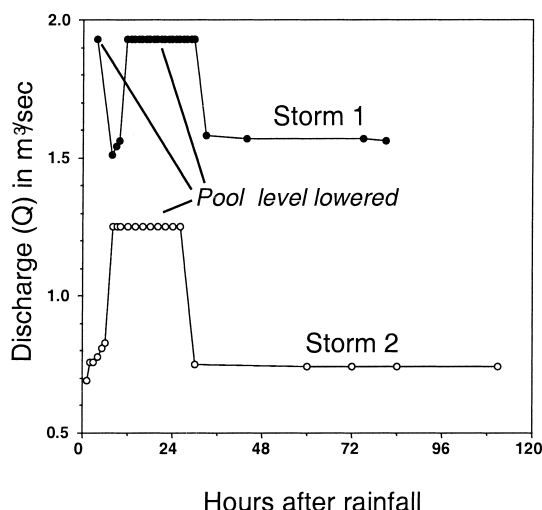


Fig. 4. Barton Springs discharge (Q) after Storms 1 and 2. Note the increase in Q in response to lowering of pool level.

EPA method A-1000; each sample was passed through a Waters Sep-Pak cartridge and analyzed using a 150×4.6 mm IC-Pak A HC column and borate/gluconate eluent. Cation concentrations were determined on a JY inductively coupled atomic emission plasma spectrometer. Cation and ion imbalance was less than 5% for all samples except one sample from Storm 2 which was therefore discarded.

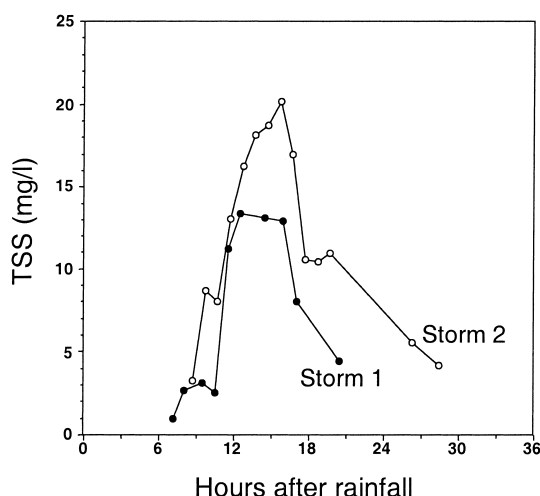


Fig. 5. Changes in TSS in response to Storms 1 and 2.

4. Results

4.1. Spring discharge and total suspended solids

Spring discharge for both storms, computed based on the rating curves developed by the USGS, is shown in Fig. 4. Draining of the pool after both storms increased spring Q considerably.

Total suspended solids, in milligrams per liter, is plotted as a function of time after rainfall (Fig. 5). For this and subsequent graphs, the time datum for Storm 1 was chosen to be the rainfall which occurred in the early morning hours of 1 November, as it greatly exceeded the rainfall of the previous afternoon. Total suspended solids began increasing about 8–9 h after rainfall and peaked about 15 h after rainfall. The shape of the curves looks much like a typical storm hydrograph, in that the rising limb is steep and the falling limb tapers off more slowly. Baseline concentrations were reached more than 30 h after rainfall. Concentrations for Storm 2 exceeded those for Storm 1. The total mass discharged in response to Storms 1 and 2 was approximately 805 and 1013 kg, respectively, calculated as

$$\sum \text{TSS}(\text{g/ml}) * Q(\text{ml/h}) \quad (1)$$

based on the time interval of sampling (approximately hourly). During the drawdown event monitored (no rainfall) turbidity remained low and constant (2–3 NTU); the amount of sediment discharging (< 1 mg/l) was insufficient for mineralogic analysis.

After filtration of particles for measurement of TSS, filter color ranged from nearly white for the first sample to a rich tan at peak TSS. Inspection of the filters under a binocular microscope revealed numerous fibers in a wide range of colors and lengths on virtually all of the filters. Filters through which DI water alone was passed did not contain the colored fibers. Some fibers were coated with what appeared to be organic matter and others were ensnared in clumps of inorganic particles and organic matter. The organic material contained was a dark brown–black; the amount appeared to increase with increasing TSS and is probably what gave the filters their tan color. Individual pieces of organic matter ranged from a few microns to $50 \mu\text{m}$ in diameter. Recognizable inorganic particles retained by the filter included quartz, calcite, and dolomite crystals. Rarer, but present, were

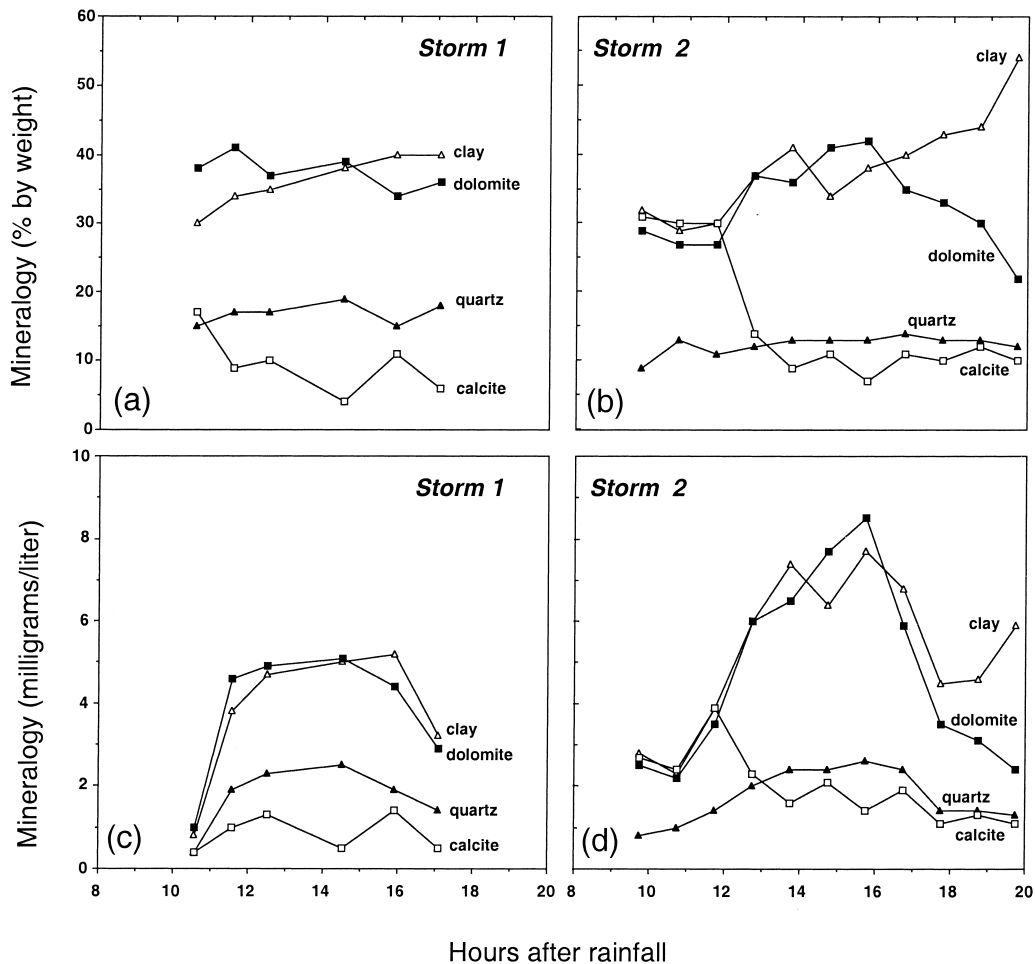


Fig. 6. Changes in mineralogy in response to Storms 1 and 2 as percent by weight of total sediment ((a) and (b)) and as concentration in milligrams of mineral per liter of sample ((c) and (d)).

colored particles 10–20 μm in diameter in shades of fuschia-pink, bright green, and turquoise blue.

4.2. Mineralogy of discharging sediments

Temporal changes in mineralogy differed between the two storms, as shown in Fig. 6. Storm 1 contained mostly dolomite and clay, with smaller amounts of calcite and quartz. The proportion of clay content increased throughout the sampling period, dolomite and calcite decreased, and quartz remained fairly constant. At the beginning of Storm 2, clay, dolomite, and calcite were present in equal proportions, with a smaller proportion of quartz. At about 12 h after

rainfall, the calcite proportion dropped to that of quartz, while proportions of clay and dolomite began to increase. Dolomite peaked at about 15 h after rainfall and then dropped, while clay continued to increase throughout the sampling period. Although samples were collected after the last times shown, not enough solids were retrieved for X-ray analysis.

4.3. Particle size distribution function

The particle size distribution function (PSDF) is expressed as the number of particles per milliliter of solution per class size ($\text{particles ml}^{-1} \mu\text{m}^{-1}$); a representative PSDF is shown in Fig. 7. Because colloidal

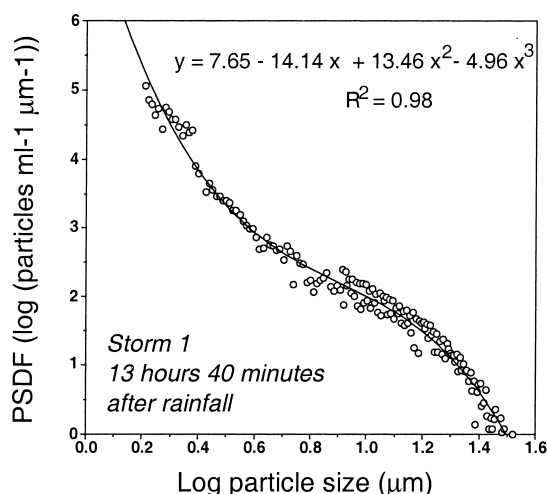


Fig. 7. Representative particle size distribution function (PSDF) fitted with a cubic model.

suspensions may evolve after collection, only those particles with a diameter (dp) $> \log 2 \mu\text{m}$ were included in the statistical analysis. Although Atteia and Kozel (1997) found a good fit with a two-part power law model, we found a cubic equation to be a better fit for our data, yielding a minimum regression coefficient (r^2) of 0.96 and in most cases > 0.99 (data not shown). The cubic model was used to calculate three representative parameters for each data set: the values of the PSDF at 4 and 10 μm ($N_{4\mu\text{m}}$ and $N_{10\mu\text{m}}$) and d_{max} , defined as the dp for which only 10 particles were counted. Changes in $N_{4\mu\text{m}}$, $N_{10\mu\text{m}}$, and d_{max} in response to each of the two storms are shown in Fig. 8. In general, after Storm 1 the number of particles in the two size ranges and d_{max} remained fairly constant after an initial increase; the maximum value of d_{max} was about 21 μm . After Storm 2, in contrast, the values of all parameters more markedly increased then decreased; d_{max} reached a maximum value of about 26 μm .

4.4. Aqueous chemistry

Changes in selected water chemistry parameters (SC, Ca^{2+} , Mg^{2+}) following both storms and drawdown are shown in Fig. 9. Both storms are displayed in terms of time elapsed after rainfall. The time datum for the drawdown was chosen to replicate that of the

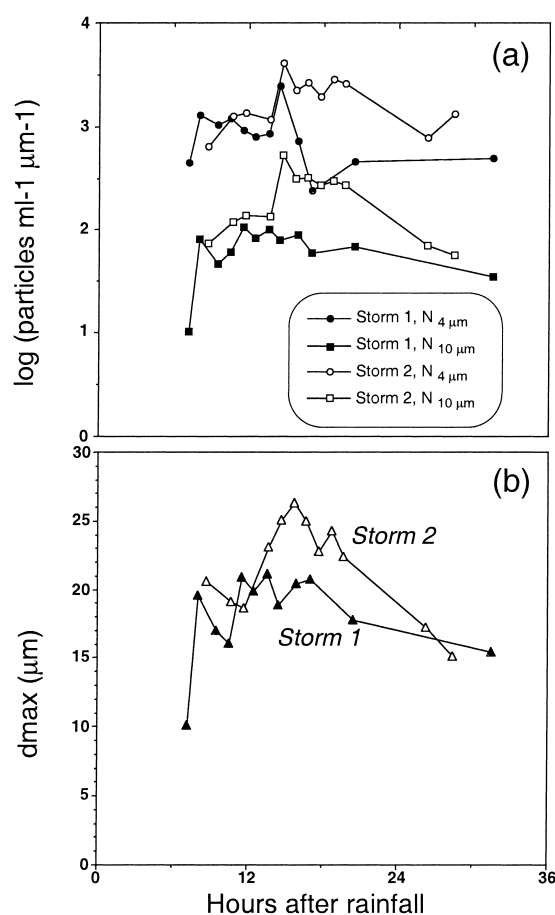


Fig. 8. Changes in PSDF parameters $N_{4\mu\text{m}}$, $N_{10\mu\text{m}}$ and d_{max} in response to Storms 1 and 2.

drawdown during Storm 2 had there been no rain. In response to Storm 1, SC (with the exception of one measurement, which may be in error) and concentrations of Ca^{2+} and Mg^{2+} decreased. After Storm 2, SC increased, reached a temporary plateau, increased more rapidly, then decreased; Ca^{2+} and Mg^{2+} increased then decreased to well below initial concentrations. In response to drawdown, SC increased slightly over a 10-h period, then increased and decreased dramatically over the following 10-h period; Ca^{2+} decreased then returned to initial concentrations, whereas Mg^{2+} remained fairly constant for the first 10 h then increased slightly over the next 10 h.

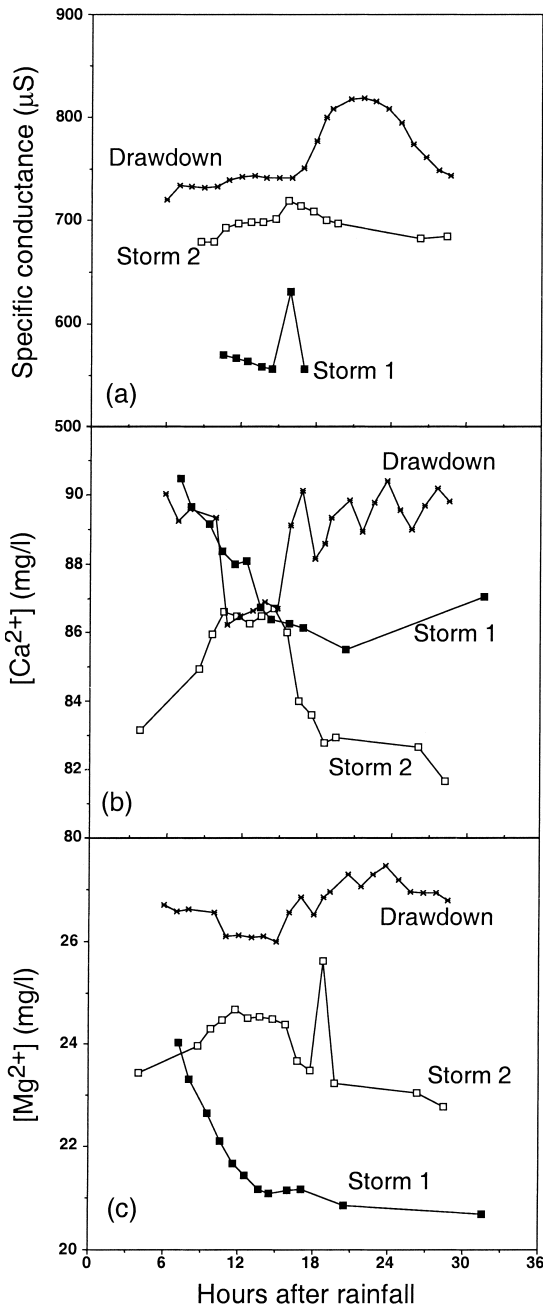


Fig. 9. Changes in chemical parameters specific conductance, calcium ion and magnesium ion in response to Storms 1 and 2 and the drawdown event.

5. Discussion

5.1. Allochthonous and autochthonous sediments

Sediments in karst originate both at the surface (allochthonous) and within the aquifer (autochthonous); allochthonous sediments filter in through openings at the surface or wash in through recharging streams, whereas autochthonous sediments are produced as internal weathering in the subsurface removes carbonate minerals, enlarging the dissolution network but leaving behind the less soluble minerals (White and White, 1968; Ford and Williams, 1989). Visual evidence and timing of sediment peaks suggest that an important fraction of discharging sediments are allochthonous.

Visual inspection of Barton Springs sediments indicated some allochthonous contribution in the form of colored fibers and organic matter. Organic matter is allochthonous. It originates from the decay of plant matter and is incorporated into the soil profile; it is also contained in domestic waste, and enters aquifers from leaking sewer lines or poorly functioning septic systems. A composite sediment sample collected from Barton Springs was found to have an organic carbon content of about 0.8% by weight, similar to that of surface sediment samples and greater than that of sediment from wells and caves (Mahler et al., 1998).

Peak concentrations of TSS discharging from Barton Springs coincide with flushing of surface water through the aquifer, as evidenced by changes in spring water chemistry. In general, for conduit-controlled karst springs the maximum dilution of groundwater by storm water recharge is seen as broad minima in SC, Ca²⁺, and Mg²⁺ (Hess and White, 1988). Arrival of surface water at Barton Springs in response to Storm 1 is indicated by decreases in SC, Ca²⁺, and Mg²⁺ (Fig. 9). When aquifer levels are at a normal level, as they were during this period, spring chemistry is not greatly affected by pool drawdown (D. Johns, unpublished data). Thus no increase in SC in response to drawdown was seen during this storm, although the decrease in SC in response to the storm may have been somewhat dampened by the effect of the drawdown. Low values of SC, Ca²⁺, and Mg²⁺ 14–15 h after rainfall coincide with peak concentrations of suspended sediment,

suggesting a surface origin for much of the suspended sediment.

In contrast, Storm 2 occurred after an extended dry period, when aquifer levels were low and pool drawdown had a pronounced effect on spring chemistry. The increase in SC caused by pool drawdown thus obscured changes in SC in response to the storm. The increases in Ca^{2+} and Mg^{2+} , however, are not responses expected from drawdown and therefore must have been caused by rainfall. This type of karst spring response to precipitation, although the opposite of that described earlier, is not unusual after a prolonged period of antecedent dryness, and is probably caused by the flushing out of water stored in the diffuse part of the aquifer by increased hydrostatic head in the recharge area (Hess and White, 1988). Thus for Storm 2, increases in Ca^{2+} and Mg^{2+} indicate arrival of stored aquifer water, and their decrease represents dilution by infiltrating surface water. Concentrations of these ions reach a maximum about 10–14 h after rainfall and a few hours before TSS peaks, and begin to decrease as TSS reaches a maximum. For this storm also the conformity between surface water arrival and suspended sediment peak suggests a surface origin for much of the sediment.

The concentration of suspended sediment discharging from Barton Springs is not directly correlated to actual spring Q . Although we would have liked to compare storm-related changes in Q to changes in TSS and aqueous chemistry, increases in Q at Barton Springs in response to the storms were obscured by far greater increases in response to pool drawdown (Fig. 4); all that can be said of these spring flow hydrographs is that springflow would have peaked at some time less than 26 h after rainfall had the pool not been drawn down. Increases in Q caused by pool drawdown do not, however, increase turbidity: during the drawdown event monitored spring turbidity remained low and constant. An increase in TSS therefore must be caused either by changes in flow conditions at the surface or in the more distal parts of the aquifer unaffected by a change in head at the spring.

Differences in the time scales of TSS and Q responses to precipitation suggest that increases in TSS are related to surface (allochthonous) rather than subsurface (autochthonous) erosion. At Barton Springs, increases and decreases in spring discharge

are generally distributed over a much longer time scale than the suspended sediment response observed here for two storms; for example, Barton Springs discharge remained high for more than three weeks after heavy rainfall in mid-May 1980 (Slade et al., 1986). After a recent rain event (6 October 1998) during which the pool was not drawn down, springflow began to increase about 1 h after rainfall, peaked about 17 h after rainfall, and very gradually decreased over a period of 10 days, still not returning to baseflow before the next rain event (US Geological Survey, unpublished data). If this can be considered representative of spring response to rainfall, peak concentrations of TSS precede peak spring flow and have a much briefer duration. In fact, the sediment “hydrograph” has a shape much more similar to that of a typical surface water storm hydrograph than that of a typical springflow hydrograph. Ryan and Meiman (1994) found a similarly brief period of sediment transport at Big Spring (Mammoth Cave National Park) despite continued high spring discharge. If most of the suspended sediment discharging from a spring is being produced by internal erosion of the aquifer, TSS should remain high as long as spring discharge is high. The rapid increase and decrease seen in TSS at Barton Springs suggests that TSS is related instead to precipitation-induced erosion at the surface or erosion of the unsaturated zone by infiltrating surface water.

5.2. Temporal changes in mineralogy and PSDF

Temporal changes in the mineralogic composition of the sediment discharging from the springs indicate varying contribution from different sediment sources. In response to both Storms 1 and 2 the proportion of clay minerals in sediment discharging from Barton Springs increased through time. This behavior, however, was not matched by equally gradual decreases in the proportions of the other three minerals present. Quartz remained at a constant proportion throughout the response to both storms. Calcite, initially present in a high proportion, dropped suddenly to a low proportion and then remained constant. The proportion of dolomite decreased throughout the response to Storm 1, but increased then decreased in response to Storm 2. Thus the increase in clay proportion cannot be solely attributed to a hydraulic change,

which would cause the small, platy clay minerals to stay in suspension as flow slows and larger particulates such as quartz, dolomite, and calcite to settle out. The varying responses in mineralogic proportions suggest, instead, that sediment source may play a role in determining the mineralogy of discharging sediments.

One cause of mineralogic variation may be accessing of different aquifer compartments at different times. Mahler et al. (1998) analyzed Barton Springs aquifer sediment mineralogy and organic carbon content and found statistically significant differences between different aquifer compartments. Sediments from surface streams, sinkholes, and small localized springs were indistinguishable, and were characterized by quartz, calcite, clay, and a fairly high organic carbon content; a second group, well sediments, were typified by a high percentage of dolomite silt and a low organic carbon content; a third group, cave sediments, contained a high proportion of clay and quartz, with a medium to low organic carbon content. Temporal variation in mineralogy of sediments discharging from Barton Springs suggests that a calcite-rich sediment source, perhaps from the surface, responds quickly to surface recharge, and that that source is then diluted by dolomite- and clay-rich sources. Although clay and dolomite proportions in the discharging sediment show similar behavior, particularly in response to Storm 2, they are unlikely to have the same source. First, well sediments containing a high proportion of dolomite contain little or no clay (Mahler et al., 1998). Second, not only do clay proportions increase as dolomite proportions decrease, which could be attributed to a decrease in flow velocity, but clay concentrations (mg/l) begin to increase toward the end of the storm response (Fig. 6(d)). The increase in clay concentrations in response to Storm 2 may be the result of sediment influx from a more distal or later-accessed source. A possible source of the dolomite is an area south of Barton Springs where dolomite silt has been filling wells (Hauwert and Vickers, 1994). Dye traces carried out during high flow conditions indicated a travel time from this area to the springs of less than 30 h (N. Hauwert, unpublished data).

A second possible cause of mineralogic variation may be mineralogic differences in surface terrain. Different members of the Edwards formation outcrop

across the aquifer, with the result that the watersheds of the six creeks contributing to the aquifer have subtly distinct mineralogies (unpub. data). Uneven mixing of watershed sediments, caused by spatial variation of rainfall, could contribute to mineralogic variation of sediments discharging at the spring.

Changes in the PSDF reflect changing hydraulic conditions within the aquifer during events. The parameters obtained from the models of the PSDF – $N_{4\mu\text{m}}$, $N_{10\mu\text{m}}$, and d_{max} – for Storm 2 in particular show clear patterns in response to the storm (Fig. 8). The numbers of particles in the 4 and 10 μm size range increase gradually; about 14 h after rainfall they increase more sharply and remain high during the period when the aqueous chemistry indicates that surface water has begun to discharge from the springs. For both Storms 1 and 2, the parameter representing the largest particle size transported, d_{max} , reaches a maximum at the same time that TSS peaks. As d_{max} is a reflection of flow velocity, this indicates that TSS is correlated with velocity within the aquifer.

The success of the PSDF parameters in characterizing particulate behavior in response to the storms was obtained through use of a closely spaced sampling interval. While the 6–12 h sampling interval used by Atteia and Kozel (1997) gives a rough description of spring response, the 1-h sampling interval used for this study results in a smooth curve describing changes in the PSDF. We obtained a better fit to the PSDF by applying a cubic equation than by applying the two-part power law employed by Atteia and Kozel (1997), however we do not suggest that the cubic equation implies any particular physical process.

The accessing of different sediment sources may be reflected in the PSDF as well as the mineralogy. Although we have treated aquifer response to the storm as lumped, different parts of the aquifer will be affected by the storm wave at slightly different times, which may be seen as slight variations within the general pattern of change within the PSDF. For example, a change in the general increase of d_{max} is seen at about the same time as changes in mineralogy: from about 8–11 h after rainfall the maximum particle size decreases, suggesting an initial influx of water from a near source, later followed by a second source (Fig. 8(b)). Further, the increase in the concentration of clay particles toward the end of response to Storm 2, suggesting an newly accessed source of clay, can

also be seen as an increase in the number of small particles ($N_{4\mu\text{m}}$) in the PSDF (Figs. 6(d) and 8(a)). Thus the PSDF may reflect sediment source as well as aquifer hydraulics.

5.3. Effects of sediment supply on discharging sediment

The concept of sediment supply used to describe and predict sediment transport by surface streams may also apply to sediment transport in karst systems. In models of surface streams, as the wet season progresses, sediment concentrations for a given stream discharge decrease as sediment supplies are depleted. During the dry period that follows, sediment supplies are “reset” by mass soil erosion processes, affected by both landuse practices (e.g. road-building, clearing of vegetation) and natural phenomena (landslides, soil creep) (VanSickle and Beschta, 1983).

Differences in the volume and mineralogy of sediment discharged in response to the two storms may be a result of seasonal differences in sediment supply. Storm 1 occurred at the end of a wet period whereas Storm 2 was preceded by a six-month dry period. Rainfall for Storm 2 was only about 75% that of Storm 1, yet the amount of sediment discharged was 125% that of Storm 1. Although this may be simply a result of location and intensity of rainfall, the qualitative difference in the amount of sediment discharged is that expected from a seasonal decline in sediment availability followed by resetting during the intervening dry period. Further, initial calcite concentrations in sediments discharging in response to Storm 2 were twice as high as they were after Storm 1. The proportion of clay to quartz also differed between the two storms, with an average of 2 : 1 in response to Storm 1 and an average of 3 : 1 in response to Storm 2.

The concept of sediment supply depletion and resetting can be more readily applied to surface sediment than subsurface sediment. Dry-season processes contributing to mass soil erosion in the subsurface are difficult to envision; if seasonal effects on sediment supply are responsible for differences in sediment discharge between Storm 1 and Storm 2, it is likely because of an effect on supply of allochthonous rather than autochthonous sediment. This in turn implies that the excess calcite and clay in the Storm 2 suspended sediments are allochthonous.

Clearly the results of two storms are not conclusive, but the possibility of a seasonal relation between TSS and spring discharge is intriguing and bears further investigation. If differences in the quantity and characteristics of sediment discharging from Barton Springs in response to Storm 1 and Storm 2 reflect seasonal differences in sediment availability at the surface, then the quantity of sediment discharging from Barton Springs will be affected by increases or changes in mass erosion processes at the surface. This could have important implications for decisions concerning land-use practices.

5.4. Implications for contaminant transport

What role might mobile sediments play in the transport of contaminants through the aquifer? Sediments adsorb and concentrate many contaminants, often in concentrations orders of magnitude greater than equilibrium concentrations of the contaminants in the aqueous phase. Our results indicate that sediments, some of them allochthonous, do move through the aquifer to exit at the springs, and thus have the potential to act as vectors for contaminant transport.

The degree to which a given contaminant will be sorbed is a function of the geochemical characteristics of the sediment. Sorption of hydrophobic organic contaminants (HOCs, e.g., petroleum hydrocarbons, PAHs, and some pesticides) is dominated by partitioning into organic carbon; allochthonous sediments, with a relatively high organic carbon content, can therefore sorb and transport HOCs. For sediments with an organic carbon content less than 0.1% by weight, sorption to the mineral surface will become the dominant sorption mechanism for HOCs and some polar organic contaminants (Schwarzenbach et al., 1993). Mobile clays, which have a large specific surface area, therefore also have the potential to concentrate and transport HOCs. Lead is another contaminant of concern in the Barton Springs Aquifer (Hauwert and Vickers, 1994). In the groundwater environment, the distribution coefficient of lead between minerals and groundwater ranges from about 30 to over 200, with sorption increasing as quartz < calcite < kaolinite (Freedman et al., 1994). Therefore while the clays have the greatest potential to sorb and transport lead, the mobile calcite and quartz sediment may also do so.

Virtually all sediment transport within the aquifer occurs during the 36 h following a storm; although the period of sediment transport is brief, the mass of sediment that is transported during that period can be substantial. Thus the effect of sediment-associated contaminant transport on water quality is likely to be most important during the early response to a storm, much like the “first flush” effect of contaminants in surface water.

The presence of a mobile solid phase capable of sorption indicates that it should be included in karst groundwater monitoring and transport models. Contaminants which are present in concentrations below detection limit in the dissolved phase can be present at concentrations many times those of suggested acceptable levels on sediments. Monitoring programs focusing only on whole water samples therefore may not detect the presence of contaminants posing a real threat to water quality.

Models attempting to characterize or evaluate contaminant transport through a karst aquifer such as the Barton Springs aquifer should take into account a mobile solid phase. The parameters needed to describe that phase include sediment density, sediment grain-size range, organic carbon content, and mineralogy. As demonstrated in this study, the concentration, mineralogy, and source of mobile sediments will vary temporally in response to a storm. Further, the quantity of sediment discharging for a given sediment may be a function of sediment supply, rather than being directly related to aquifer discharge.

6. Conclusions

This investigation demonstrates that sediments are mobile in a karst aquifer, that they can enter from the surface and traverse the aquifer to discharge at a spring, and that virtually all sediment transport occurs immediately following storm events. In the Barton Springs aquifer, approximately a metric ton of sediments discharged from Barton Springs in the 24 h following each of two major storm, with peak concentrations of suspended sediments of 13–20 mg/l occurring 15–16 h after rainfall. The maximum particle size transported coincided with the peak in TSS. A

closely spaced sampling interval allowed the fine description of changes in mineralogy and particle size distribution of the sediment.

Both allochthonous and autochthonous particles are transported through the aquifer. Organic carbon and colored fibers were visible on filters after filtration of spring discharge. The peak concentration of TSS coincided with the arrival of surface water, evidenced after a wet season storm by a drop in specific conductance, and after a dry period by a decrease in Ca^{2+} and Mg^{2+} following an initial increase. Differences between the amount and character of sediment discharging in response to the two storms suggest that a sediment supply model usually applied to surface streams may also apply to this spring system; this model requires that sediment supplies are “reset” during a dry season by mass erosion processes at the surface.

The mineralogy of discharging sediments changed over the course of both storm responses. Changes in the proportions of minerals (calcite, dolomite, quartz, and clay) suggest that different sediment sources or compartments are accessed at different times. Temporal changes in the maximum particle size transported were consistent with this hypothesis.

The large quantity of sediment flushing through the aquifer indicates that mobile sediments have the potential to play an important role in the concentration and transport of contaminants. Allochthonous sediment in particular, which may be exposed to contaminants at the surface and can have a relatively high organic carbon content, may be a significant source of groundwater contamination. Mobile particulates, therefore, should be included in both karst groundwater monitoring programs and contaminant transport models.

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